

DEFINITIVE AGREEMENT

Agreement made as of this 1st. day of July, 1980 between CELANESE CORPORATION, a Delaware corporation, and its wholly-owned United States subsidiaries, including Celanese Chemical Company, Inc., a Texas corporation, all hereinafter referred to as "Celanese"; and REDOX TECHNOLOGIES INC., a New Jersey corporation, hereinafter referred to as "Redox".

SECTION 1

As used in this Agreement:

1.1 The term "Field" shall mean processes for the manufacture of ethylene glycol (EG) involving a series of steps as follows:

- A. The manufacture of tertiary butyl hydroperoxide (TBHP) by the reaction of isobutane and oxygen,
- B. The manufacture of di-tertiary butyl peroxide (DTBP) by the reaction of TBHP and isobutylene,
- C. The manufacture of EG as well as the simultaneous manufacture of coproducts including glycerine, t-butanol, acetone and others by the free radical

If to Redox, to:

Redox Technologies, Inc.
6 Spencer Court
Wyckoff, New Jersey 07481

Attention: President

If to Celanese to:

Celanese Chemical Company, Inc.
P.O. Box 47320
1250 W. Mockingbird Lane
Dallas, Texas 75247

Attention: President

with a copy to:

Celanese Corporation
1211 Avenue of the Americas
New York, New York 10036

Attention: Secretary

- 7.4 The validity, performance, construction and effect of this Agreement shall be governed by the laws of the State of New York.
- 7.5 This Agreement shall be binding upon the successors or permitted assigns of either party hereto, but shall not be assignable by either party without the written consent of the other except that Celanese may without consent assign this Agreement to a transferee of its entire EG business activities.
- 7.6 The parties agree to take no action which would violate the laws or regulations of any country, including but

not limited to the United States Export Administration
Act of 1979 (PL 96-72).

CELANESE CORPORATION

REDOX TECHNOLOGIES, INC.



Signed 1-7 1981

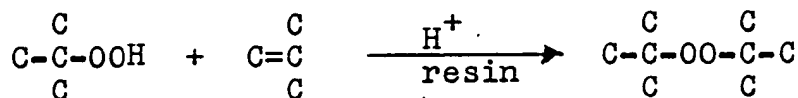
Signed 12-22- 1980

11/20/80-FK

Alkylation Of t-Butyl Hydroperoxide With Isobutylene

The alkylation of t-butyl hydroperoxide with isobutylene either pure or contained in a mixed butene stream is a very facile reaction which is acid catalyzed. Most of our work has been conducted with pure isobutene, with a limited amount of work done with normal butenes alone to establish that a nil amount of alkylation is occurring. Alkylation is effected by strong acid ion exchange resin of the sulfonic acid type preferably with the macro recticular structure that is most beneficial for organic reactions. Other solid acids are also effective and do not require the removal of the organics by distillation which is our preferred operating conditions. The reaction appears to be first order with respect to isobutylene, t-butyl hydroperoxide and acid.

$$r = k \left[iC_4^- \right] \cdot \left[tBHP \right] \cdot \left[H^+ \right]$$



Our alkylation is based on the following design case shown in Table 3.

Table 3

Alkylation Of t-Butyl Hydroperoxide Design Case

Temperature	50-70°C
Pressure	200 psig
Catalyst	H ⁺ resin
tBHP:iC ₄ ⁻ : nC ₄ ⁻ : tBA (molar)	1.03:1.0:1.0:.51
WHSV	1.0 hr ⁻¹
Conversion M%	
t-butyl hydroperoxide	95
isobutylene	98
Selectivity mol %	
di-t-butyl peroxide	≈ 100°

The use of a 50-50 isobutylene n-butene stream is an arbitrary selection and in fact would be any stream with contained isobutylene that is available. The use of pure isobutylene is undesirable from a cost viewpoint since it is generally almost 50% more costly than a contained isobutylene stream. If the desire to hold down the product output becomes important then of course some of the indigenously produced tert butanol is readily dehydrated to a high quality isobutylene.

The world has a shortfall of gasoline and the gasoline market is demanding greater octane rating of the clear gasoline as the lead is being removed. It is absolutely clear and demonstrated by fact that where possible the volatile non-gasoline components are being converted to high octane less volatile components for gasoline. Methyl t-butyl ether from isobutylene and methanol is a case, in point as is the isobutane to t-butanol transformation. The use of other oxygenated have been announced and the use of ethanol (fermentation) has also recieved a great play. Since the formation of the di-t-butyl peroxide is a necessary part of the process, it is inconceivable that there would exist any logic not to benefit from this necessity.

t-Butyl hydroperoxide alkylation with isobutylene shows a reaction rate constant much greater than the rate constant of alkylation of either water or methanol. As a consequence of this high rate constant, the side reaction of self alkylation to disiobutylene and more complete utilization of the contained isobutylene should be possible in this system than in the alkylation of methanol. We have not established the levels of disiobutylene that is present in our alkylation nor have we sought to demonstrate the lowest level of isobutylene that can be present at acceptable rates of formation of di-t-butylperoxide.

Our projections based on MtBE literature is that our di-t-butyl peroxide effluent should contain about .1% or less disobutylene and .1% or less of butenes, while obtaining about 98-99% conversion of the contained isobutylene. Thermal studies conducted on tBHP in the presence of acid ion exchange resin show that there is virtually no decomposition at 60°C and a residence time of 1 hour at concentrations similar to our design. Di-t-butyl peroxide is also stable at these conditions.

Slight amounts of other alkylated products will be made by the reaction of isobutylene with MeOH and with organic acids. If water were present, this too could react to yield t-butanol.

Engineering Safety and Environmental

The design of Section 200 is based on the kinetics of the reaction which mandates that a plug flow reactor be used to attain the highest possible level of conversion of both the t-butyl hydroperoxide and isobutylene. We chose as the terminal point of the reaction a conversion of 95% of the t-butyl hydroperoxide and a 96 to 98% conversion of the contained isobutylene. Looser requirement on either of these conversion factors can of course increase productivity of DtBP.

There are a number of approaches for the design of this alkylator. We have chosen a tube in a shell configuration with about 320-12' Schedule 40 carbon steel pipes of 45 ft. length in a shell of carbon steel. The tubes are filled with ion exchange resin and the reactants flow upward through the tubes while cooling water flows concurrently outside the

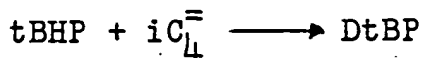
tubes. This scheme provides maximum cooling during the earliest part of the reaction which evolves the most heat of reaction. DtBP is a more stable entity than tBHP to temperature and most every other catalyst including acids. For this reason we would prefer maximum reaction to occur at milder conditions than 60°C where the kinetics are favorable. The final portions of the reaction, we seek to push to completion, is then conducted at a somewhat higher temperature of about 70°C where the reaction rate constant is greater, but the possibility of loss of active components is minimized.

Alternative approaches for this design are use of a packed bed reactor with multiple withdrawal and injection points to provide cooling and the use of a back mixed reactor cooled by normal means where a high percentage of the reaction is completed, followed by an adiabatic tubular plug flow reactor. In any of these systems the effluent should be monitored for strong acid and neutralized by weak salts if any is present. Data in Table 4 is used in the design of Section 200.

Table 4

Alkylation - Physical Properties

Heat Of Reaction



$$H = -22,100 \text{ BTU/mol/lb.}$$

Heats Of Vaporization

n-butene	C_4H_8	MW 56	11,400 BTU/mol/lb.
isobutylene	C_4H_8	MW 56	10,427 BTU/mol/lb.
t-butanol	$\text{C}_4\text{H}_{10}\text{O}$	MW 74	18,910 BTU/mol/lb.
acetone	$\text{C}_3\text{H}_6\text{O}$	MW 58	13,877 BTU/mol/lb.

Alkylation - Physical Properties (cont'd)

Vapor Pressure

$$\text{Log}_{10} P = (-.2185 A/K) + B$$

K = ° Kelvin

P = mm Hg

	A	B
n-butene	622.6	7.882542
isobutylene	5742.9	7.601563
t-butanol	10413.2	9.193472
acetone	7641.5	7.904024

Heat Capacities

n-butene	.94 BTU/lb/°C
isobutylene	.939 BTU/lb/°C
t-butanol	1.31 BTU/lb/°C
acetone	.946 BTU/lb/°C

The butenes including unreacted isobutylene is removed in a two column configuration. The first column is a pressure distillation to remove the bulk of the butenes in a condensed phase, followed by a stripper column designed for maximum removal of butenes. The butenes overheads are compressed in a reclaim compressor and sent back to an upper tray in the butenes column.

At this point in time we do not envision a need to purify the DtBP by distillation. This is possible if the need for it should be established.